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(19) (CA) **CANADIAN PATENT** (12)

(54) PROCESS FOR PRODUCTION OF FINELY DIVIDED
MAGNETITE PARTICLES

(70) Kunda, Wasyl; Rudyk, Boris,
Canada

Granted to Sherritt Gordon Mines Limited,
Canada

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A B S T R A C T

Finely divided particles of magnetite are produced by mixing solutions containing ferrous ions, ferric ions and free ammonia in proportions necessary to neutralize any free acid. The mixture is maintained at a temperature of at least 50°C. Magnetite particles precipitate from the mixture and may be recovered by conventional liquid-solid separation procedures.

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This invention relates to a process for the production of fine particles of magnetite suitable for use in magnetic tapes and ink and the like. More particularly, the invention relates to a process which involves reacting
5 ferrous and ferric salts, and ammonia under controlled conditions in an aqueous medium to cause precipitation of spheroidal, fine particles of magnetite.

It is known to prepare particles of magnetite by subjecting iron powder to partial oxidation or by subject-
10 ing particles of hematite to partial reduction. The magnetite particles thus produced are too coarse for use in magnetic inks and must be pulverized by some means. The means conventionally used for doing so is wet grinding in a ball mill. However, grinding must be continued for a
15 very long time, frequently as long as 1,000 hours, to decrease the state of subdivision of the particles to that suitable for use in magnetic ink. Because of the prolonged grinding required, the cost of the grinding operation is considerable and usually accounts for a substantial portion
20 of the overall cost of production of the magnetite particles.

It is an object of the present invention to provide a process by which spheroidal magnetite particles suitable for use in magnetic inks and tapes can be produced but which does not involve grinding the particles.

25 It is another object to provide a process by which the size of magnetite particles can be controlled within the range of 200 to 500⁰A by simple and inexpensive means.

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These and other objects may be accomplished by a process which involves providing solutions containing ferrous ions, ferric ions, and free ammonia; mixing said solutions in proportions necessary to neutralize any free acid; maintaining the temperature of the mixture at at least 50°C to cause a reaction therein with resulting formation of finely divided particles of magnetite; and recovering said magnetite particles.

10 The process of the invention is described below with reference to the drawings in which:

Figure 1 is a graph showing the effect of the mixing sequence of ammonia and aqueous solutions of ferrous and ferric sulphate on the settling rate of magnetite precipitated from the resulting slurry; and

20 Figure 2 is a graph showing the effect of the $\text{Fe}^{+++}/\text{Fe}^{++}$ molar ratio on the settling rate of magnetite from a slurry of ferrous hydroxide and ammonia to which is added an aqueous solution of ferric sulphate.

As starting materials for the process of the subject invention, solutions containing free ammonia and dissolved salts of di- and tri-valent iron are required. Three separate solutions may conveniently be used for the purpose, one a solution which contains ferrous ions (for the sake of brevity referred to below as solution 1), a solution which contains ferric ions (solution 2) and a solution which contains free ammonia (solution 3). Solutions
30 (1) and (2) may be derived from the combination of iron

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values and one or more of the common acids in which the iron values are soluble. The acid may, for example, be sulphuric acid, hydrochloric acid and acetic acid.

The first step of the process involves mixing solutions (1), (2) and (3) in such quantities that all free acid in solutions (1) and (2) are neutralized by the free ammonia in solution (3). In addition, it is preferred that solutions (1) and (2) be combined in such proportions that the ferric to ferrous molar ratio in the resulting mixture be in the range of 3:1 to 1:1 and more preferably 2:1. It is also preferred that solutions (1), (2) and (3) be so combined that the concentration of soluble iron values in the mixture be in the range of 10 to 30 g.p.l.

The most convenient method for determining the correct amount of solution (3) which must be combined with solutions (1) and (2) to neutralize all free acid is to monitor the pH of the resulting mixture. All free acid will be neutralized when the pH of the mixture is the same or higher than the pH of the iron salt resulting from the reaction between the iron values and the acid in solutions (1) and (2). For example, should the acid in solutions (1) and (2) be sulphuric acid, a sufficient quantity of solution (3) should be added to increase the pH to at least 5.4 which is the pH of iron sulphate in solution. Similarly, should the acid be acetic acid, solution (3) should be added in sufficient quantity to increase the pH to that of iron acetate in solution. In cases where the form of the iron salt in solutions (1) and (2) is unknown because, for example, the acid make-up of solutions (1) and (2) is undetermined, the quantity of solution (3) with

solutions (1) and (2) should be that required to raise the pH to about 7. It is possible to raise the pH to a higher value but it is preferred not to do so because of the added cost of handling a more basic mixture and because
5 of the tendency of the magnetite formed in the mixture to oxidize to iron hydroxide.

As indicated above, it is preferred to maintain the $\text{Fe}^{+++}/\text{Fe}^{++}$ molar ratio in the mixture resulting from the combination of solutions (1), (2) and (3) within the
10 range of 3:1 and 1:1. Where the molar ratio is outside this range, undesirably large quantities of iron hydroxide are formed in the mixture with resulting lowering of the magnetic properties of the end product of the process. It should be noted, however, that the lowering of magnetic
15 properties is more pronounced where the ferric to ferrous molar ratio is below 1:1 than where it is above 3:1.

In general, the overall concentration of iron in the mixture has no effect on the formation of magnetite. However, an iron concentration below about 30 g.p.l. favours
20 production of a finer magnetite product than a higher concentration of iron. Since a finer product is generally more useful than a coarser product, it is preferable to maintain the concentration of iron below 30 g.p.l.

The sequence of mixing solutions (1), (2), and (3)
25 has a significant effect on the quantity of magnetite produced by the subject process. The mixing of ferrous solution (1) and ferric solution (2) and the addition of the resulting mixture to ammoniacal solution (3) causes an immediate reaction in which substantially all iron values
30 present in the mixture or slurry convert to magnetite.

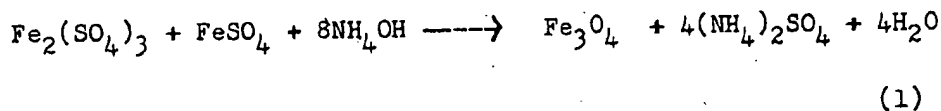
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Even more rapid and complete conversion of the soluble iron values to magnetite occurs when the ferrous-ferric mixture is sprayed into ammoniacal solution (3).

5 The addition of ammoniacal solution (3) to a ferrous-ferric solution (1) (2) results in the precipitation first of brown $\text{Fe}(\text{OH})_3$, then the precipitation of green $\text{Fe}(\text{OH})_2$ and finally, magnetite. However, conversion of $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$ to magnetite is incomplete. The addition of ferrous solution (1) to ammoniacal solution (3) 10 and afterward the addition of ferric solution (2) to the resulting ferrous ammoniacal solution (1) (3) results first in the precipitation of $\text{Fe}(\text{OH})_2$ and afterward the precipitation of magnetite but again conversion to the latter compound is incomplete. Similarly, the addition of ferrous solution (1) 15 to a combined solution (2) and (3) results in the incomplete conversion of soluble iron values to magnetite.

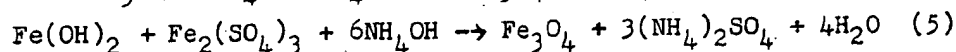
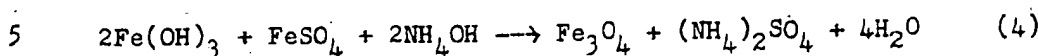
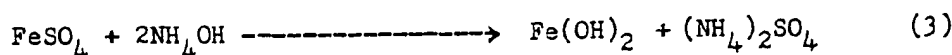
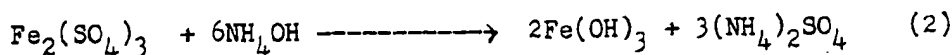
The temperature of the mixture or slurry resulting from the combination of solutions (1), (2) and (3) should be maintained at at least 50°C and preferably should be main- 20 tained at a temperature within the range of from about 100 to 150°C . Maintaining the temperature near the upper limit of this range results in a magnetite end product which is denser and which has a smaller surface area than the end product produced at a lower temperature.

25 The reaction which is believed to occur in the mixture or slurry is as follows (where solutions (1) and (2) contain sulphuric acid):



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Besides this reaction, other side reactions are also believed to take place, they being:



As evident from the above equations, ammonia is essential to precipitation of magnetite. The minimum quantity of ammonia required is the stoichiometric equivalent of the quantity of sulphate sulphur present in the combined solution. Thus 2 moles of ammonia are required for each mole of sulphate sulphur present. Ferric sulphate and ferrous sulphate solutions accordingly require 3 and 2 moles of ammonia per mole of iron respectively. In addition, 2 moles of ammonia are required for each mole of free sulphuric acid present in the combined solution. As previously indicated, the most convenient method for ensuring that sufficient ammonia is present in the mixture or slurry resulting from the combination of the three solutions is by monitoring the pH thereof. When the pH is 5.4 or higher, no further ammonia need be added.

In general, agitation of the mixture results in a finer product; thus, the size of the final product can be, to a certain extent, controlled by the extent to which the mixture is agitated during the reaction.

Various so-called "surface active agents" may be added to the mixture to control the shape and size of the precipitated magnetite particles. Agents suitable for the purpose are those identified by the trade marks Goulac, Dextrin, Orzan, Tween 60, EMA-1103, Span 85 and Aerosol C-61. Usually a concentration of about 0.5 g.p.l. of the agent in the mixture is sufficient for the purpose.

At the completion of the reaction, the magnetite particles may be separated from liquid by filtration and may be dried by conventional means. During drying, the particles usually agglomerate but in most cases the
 5 agglomerates may be broken down without difficulty. For example, where the particles are washed with water and dried at 100°C, they agglomerate into a very brittle lump but the lump can be easily broken down by grinding. Where the particles are washed in acetone and dried in a vacuum,
 10 they agglomerate into a soft product which again may be broken down without difficulty.

The resulting magnetite particles are generally spheroidal in shape and are within the size range of about 200 to about 500 Å. The particles may be somewhat contaminated with iron hydroxide which can be converted to magnetite by heat treatment in a neutral atmosphere.
 15

EXAMPLE 1

This example illustrates the effect which the sequence of mixing the ferrous solution (1), ferric
 20 solution (2) and ammoniacal solution (3) has on the settling rate of precipitated magnetite. Samples of such solutions were mixed in various sequences to form a number of charges, each 700 ml in volume and containing 10 g.p.l. iron. The molar ratios of Fe^{++} , Fe^{+++} and NH_3 in the charges were:
 25 $\text{Fe}^{+++}/\text{Fe}^{++} = 2:1$ and $\text{NH}_3/\text{Fe}_T = 4:1$. To some charges were added 0.5 g.p.l. EMA-1103, to others none. The charges were maintained at a temperature of 50°C for an hour each.

Figure 1 illustrates the effect of the mixing sequence on the settling rate of precipitated magnetite.
 30 The figure clearly shows that the settling rate is slowest

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where the mixing sequence is solutions (1) and (2) added to solution (3) and is fastest where the mixing sequence is solution (1) added to a mixture of solutions (2) and (3). It is believed that the solid product from the former mixing sequence settles more slowly than the product from the latter mixing sequence because the former product is significantly finer than the latter product. Since a finer product is preferred, the former mixing sequence is preferred.

EXAMPLE 2

This example illustrates the effect of the $\text{Fe}^{+++}/\text{Fe}^{++}$ molar ratio on the settling rate of precipitated magnetite. 700 ml samples were prepared by adding various amounts of a solution containing ferric ions to a solution containing free ammonia and ferrous ions. The total concentration of iron in the samples was approximately 10 g.p.l. and the NH_3/Fe_T molar ratio was 4. The surface activator EMA-1103 was added to some of the samples.

The samples were maintained at a temperature of 50°C for a period of time and the settling rate of magnetite from the samples was determined by periodically measuring the height of the zone of clear solution above the dark magnetite-containing slurry. The results are shown in Figure 2.

From Figure 2 it is clear that the fastest settling rate occurs when the $\text{Fe}^{+++}/\text{Fe}^{++}$ ratio is 3:1 and the slowest rate occurs when the ratio is 1:1. The slow settling rate is believed to be due to the presence of $\text{Fe}(\text{OH})_2$. Magnetite particles precipitated from samples containing EMA-1103 settled more slowly indicating that the particles were probably somewhat finer than magnetite particles precipitated from samples lacking the surface activator.

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The embodiments of invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for producing finely divided particles of magnetite comprising: providing solutions containing ferrous ions, ferric ions and free ammonia; mixing said solutions in proportions necessary to neutralize any free acid; maintaining the temperature of the mixture at at least about 50°C to cause formation of finely divided particles of magnetite; and recovering said magnetite particles.

2. The process as claimed in claim 1 wherein the ratio of ferric ions to ferrous ions in said solutions is in the range of from about 3:1 to about 1:1.

3. The process as claimed in claims 1 wherein the ratio of ferric ions to ferrous ions in said solutions is 2:1.

4. The process as claimed in claim 1 wherein the concentration of iron in said solutions is in the range of about 10 to about 30 g.p.l.

5. The process as claimed in claim 1 wherein the temperature of said solutions is maintained within the range of 100 to about 150°C.

6. The process as claimed in claim 1 wherein said mixture also contains a surface active agent selected from the group consisting of Goulac, Dextrin, Orzan, Tween 60, EMA-1103, Span 85 and Aerosol C-61.

7. A process for producing finely divided particles of magnetite comprising: providing a slurry derived from the combination of divalent and trivalent iron values dissolved in an acidic medium and sufficient ammonia to adjust the pH of the liquid in said slurry to that of an iron salt resulting from the reaction between said iron values and the acid; maintaining said slurry at a temperature of at least 50°C to cause formation of finely divided particles of magnetite; and recovering said magnetite particles.

8. A process for producing finely divided particles of magnetite comprising: providing (a) a starting solution containing ferrous ions and ferric ions in an acidic medium and (b) an ammoniacal solution; adding solution (a) to a sufficient quantity of said solution (b) such that all free acid in the resulting slurry is neutralized; maintaining said slurry at a temperature of at least about 50°C to cause formation of finely divided particles of magnetite; and recovering said magnetite particles.

9. The process as claimed in claim 8 wherein solution (a) is added to solution (b) by spraying.

10. The process as claimed in claims 7, 8 or 9 wherein the ratio of ferric ions to ferrous ions in said acidic medium is in the range of from about 3:1 to about 1:1.

11. The process as claimed in claims 7, 8 or 9 wherein the ratio of ferric ions to ferrous ions in said acidic medium is 2:1.

12. The process as claimed in claims 7, 8 or 9 wherein the concentration of iron in said acidic medium is in the range of about 10 to 30 g.p.l.

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13. The process as claimed in claims 7, 8 or 9 wherein the temperature of said acidic medium is maintained in the range of about 100 to about 150°C.

14. The process as claimed in claims 7, 8 or 9 wherein said slurry also contains a surface active agent selected from the group consisting of Goulac, Dextrin, Orzan, Tween 60, EMA-1103, Span 85 and Aerosol C-61.*

15. The process as claimed in claims 7, 8 or 9 wherein said acidic medium is sulphuric acid and the pH to which said slurry is adjusted is at least about 5.4.

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2-1

EFFECT OF MODUS OF MAGNETITE
PRECIPITATION ON SETTLING;

CONDITIONS: 50°C; 10gpl IRON; NONE OR 0.5gpl EMA-1103;
Fe⁺⁺⁺/Fe⁺⁺ MR= 2/1; NH₃/Fe MR=4/1;
700ML CHARGE IN BEAKER.

MODUS OF SOLUTION MIXING:

- (a) AMMONIA ADDED TO THE MIXTURE OF
Fe⁺⁺⁺ & Fe⁺⁺ SOLUTIONS.
- (b) Fe⁺⁺⁺ & Fe⁺⁺ SOLUTIONS ADDED TO AMMONIA SOLUTION
- (c) Fe⁺⁺⁺ SOLUTION ADDED TO MIXTURE OF
Fe⁺⁺ & AMMONIA SOLUTIONS.
- (d) Fe⁺⁺ SOLUTION ADDED TO A MIXTURE OF
Fe⁺⁺⁺ & AMMONIA SOLUTIONS.

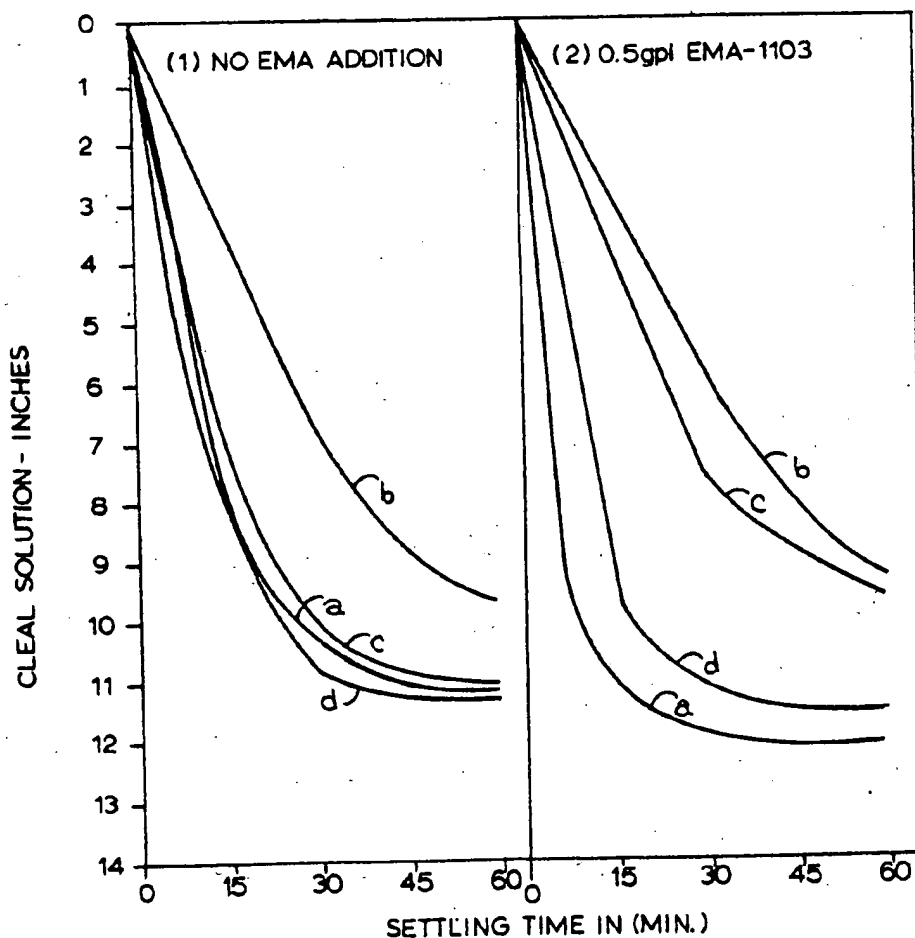


FIG. 1

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2-2

EFFECT OF $\text{Fe}^{+++}/\text{Fe}^{++}$ MOLAR RATIO ON
SETTLING OF MAGNETITE (1) IN ABSENCE OF
EMA-1103; AND (2) IN THE PRESENCE OF EMA-1103

CONDITIONS: 50°C; 10gpl IRON; NH_3/Fe MR=4;
 METHOD-C; 700ML CHARGE IN THE BEAKER.

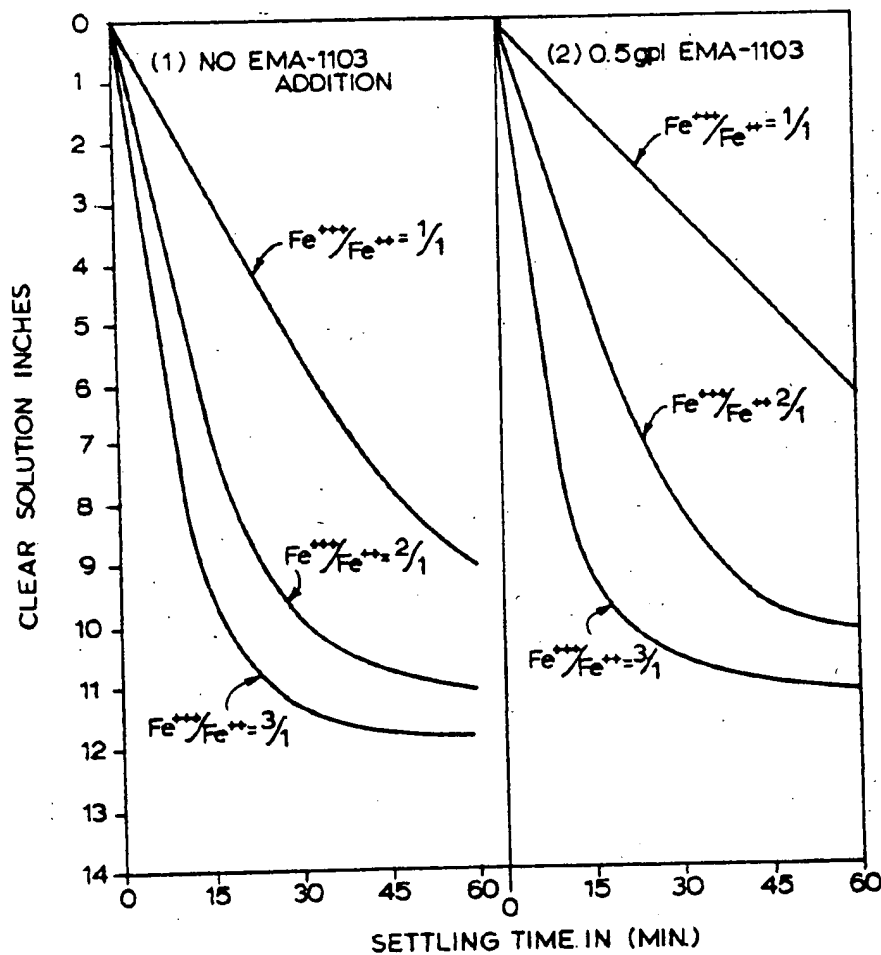


FIG. 2

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